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ABSTRACT

Waterborne polyurethanes (WBPUs) have attracted increasing attention in a wide range of industrial applications because of their versatile properties as well as ecofriendly nature. Although extensive research has been carried out on WBPU synthesis, the roles of some of the key synthesis components remain unclear. In this study, through systematically controlling and fine tuning the precursor compositions and reaction conditions, we have synthesized over 300 WBPUs. This research enabled us to identify the roles of several key components that govern WBPU physicochemical properties and ultimately the potential WBPU applications. Using hair styling as an example, we demonstrate that only the WBPUs with an optimal range of properties (e.g., Young's modulus > 150 MPa, Elongation at break: 15-300%, moisture uptake < 10%) can achieve strong styling performance. To further improve the natural-feel sensory benefits in the final styling products, a number of fatty acids with different carbon chain lengths or unsaturation levels were incorporated into WBPUs. Among ten fatty acids studied, linoleic acid was identified as the most preferred additive. Both *in vitro* and *in vivo* testing demonstrated that WBPUs with optimal properties are promising materials for developing strong, long lasting styling products with natural feel.

Polyurethanes are versatile materials that have been used in a wide range of industrial applications including biomedicine, building and construction, automotive, textiles, and personal care.[1, 2] In particular, waterborne polyurethanes (WBPUs) have emerged as a new technology for creating ecofriendly adhesives and coatings because they are non-toxic and non-flammable.[3] A WBPU dispersion consists of polyurethane polymer chains dispersed in water; therefore, its properties are largely determined by the chemical composition of the polymer building blocks. The main components that are used for WBPU polymer synthesis (polyols, diisocyantes, diols, neutralizers, hydrophilic chain extenders, and additives) all play important roles in determining the structure and properties of WBPUs. Although extensive research has been carried out to understand the roles of some of these key components, different or even contradictory results are often reported in the literature. These differences arise due to the use of different synthesis methods and functional groups, and thus make study-to-study comparison difficult. For example, Tanaka et al. reported that polycarbonate-based WBPUs provided higher Young's modulus (Y_M) compared to polyether-based WBPUs,[4] while Garcia-Pacios et al., showed that polycarbonate-based polyurethanes had lower Y_M compared to polyether/polyester based polyurethanes.[5] To better understand the specific roles of these key parameters, systematic synthesis of WBPUs should be performed in which single variables are isolated. In the present study, over 300 WBPU materials have been synthesized with systematic tuning of the concentrations of various components, allowing us to understand the specific role that each of these components plays in governing WBPU physicochemical properties. Using hair styling as an example, we demonstrate that only WBPUs with optimal mechanical properties and hydrophobicity can achieve strong styling performance, and that

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the encapsulation of select fatty acid-based additives further improves the sensory benefits of the WBPU styling polymer. Both *in vitro* and *in vivo* testing show that these WBPUs are promising materials for strong, long-lasting styling products with natural feel.

The primary monomers used in WBPU synthesis are polyols, diisocyanates, and chain extenders. In this study, a large number of syntheses have been carried out to understand the roles of some of these key components. Sodium carbonate (Na_2CO_3) was selected as the preferred neutralizer due to its relatively benign safety profile.[6] Three different polyols have been explored: polyether, hexanediol-based polycarbonate, and hexanediol/pentanediol-based polycarbonate, each with concentrations varied from 30 to 65 wt%. Our preliminary results show that all three polyols had a similar impact on WBPU mechanical properties; however polycarbonate-based polyols yielded polyurethanes with higher Y_M compared to those made from polyether-based polyols or hexanediol/pentanediol-based polycarbonate polyols. The higher Y_M for the polycarbonate-based WBPUs was likely due to the additional hydrogen bonding between the carbonyl groups of the soft segment.[7] This is consistent with the report by Tanaka and colleagues that demonstrated that additional hydrogen bonding from polycarbonate polyols resulted in better phase mixing, corresponding to improved mechanical properties.[4]

Two chain extenders were employed to increase the WBPU molecular weight: 1,4-butanediol and L-lysine. The former reacts with isocyanate functional groups to form urethane bonds, whereas the latter reacts with isocyanate groups to form urea bonds.[8] The molar ratio between isocyanate functional groups and the sum of hydroxyl and amine groups was kept at 1:1 for all syntheses; for example when polyol content was held constant and the concentration of L-lysine increased, the concentration of 1,4-butanediol decreased accordingly. **Figure S1** shows that the mechanical

properties of WBPUs can be tuned in a wide range by adjusting the L-lysine concentration: as the L-lysine concentration was increased from 0 to 12 wt%, a gradual decrease in the Elongation at Break (E_B) was observed; similarly, Y_M gradually increased with increasing L-lysine concentration until it reached maximum at a 8 wt% L-lysine concentration. This effect is likely because the stronger cohesive forces between urea bonds as compared to urethane bonds lead to more robust materials. A similar effect has been reported for other diamine chain extenders.[9] **Figure S1** suggests that a L-lysine concentration of 4-6 wt% is preferred if one wants to create a strong but rather flexible polyurethane material. The presence of ionizable functional groups in L-lysine is also expected to improve the stability and thus shelf life of WBPU dispersions.[10]

Diisocyanate monomers also play an important role in determining WBPU physicochemical properties. In the present study, two different isocyanates were explored in order to optimize polyurethane properties for hair styling applications: isophorone diisocyanate (IPDI) and 4,4'-dicyclohexylmethane diisocyanate ($H_{12}MDI$). It has been reported that $H_{12}MDI$ usually results in polyurethanes with more ordered crystalline domains and thus forms materials of greater tensile strength and hardness.[1] For fair comparison, syntheses of WBPUs with the same molar concentration of IPDI and $H_{12}MDI$ were performed. Transmission electron microscopy (TEM) analysis revealed that the WBPU dispersions synthesized with $H_{12}MDI$ consisted of larger particles (**Figure 1a**). X-ray diffraction analysis (XRD) shows that both dispersions exhibited a strong characteristic peak at 19.8° 2θ and a weak shoulder at 42-43° 2θ (**Figure 1b**).[11] However, the 19.8° 2θ peak was more distinct in the $H_{12}MDI$ sample, suggesting a relatively higher degree of orientation within the structure and thus more crystalline domains within this material.[12] No significant differences in the mechanical properties were observed (**Table S1**). This unexpected result may arise from presence of

multiple isomers (trans-trans, cis-trans, cis-cis) within H_{12}MDI used in this study. Saralegi et al. reported that the isomer composition of H_{12}MDI greatly affected the final mechanical properties of WBPUs.[12] The trans-trans isomer provides more efficient packing and improved phase separation within the WBPU, and as the concentration of this isomer increased, both Y_M and E_B dramatically increased. However, different results may be expected when a mixture of isomers is used. For example, Barikani et al. found that the tensile strength was slightly lower for H_{12}MDI-based WBPUs as compared to IPDI-based WBPUs,[13] and Hourston et al. reported that H_{12}MDI based polyurethanes not only showed lower tensile strength but also smaller particle size.[14] Hence, the similar mechanical properties of IPDI-based and H_{12}MDI-based WBPUs observed in this study likely arose from the use of mixed H_{12}MDI isomers.

Once we understand the specific role that each of these components plays in determing WBPU properties, we can further tailor the system and perform fine-tuning towards certain specific applications. Using hair styling as an example, we know that one of the most common needs in hair styling is a strong hold without stickiness and superior humidity resistance, which would translate to WBPU polymers with an optimized balance of different properties.[15, 16] By establishing a large WBPU library comprising over 300 materials, we were able to identify three key properties that govern WBPU styling performance: mechanical properties (Y_M, E_B, and Ultimate strength (U_S)), hydrophobicity (the hydrophobicity of WBPUs is evaluated based on the moisture uptake of the cast films), and sensory attributes. **Figure S2** shows the physicochemical properties of 135 representative WBPUs explored in this study. It is clear that all properties can be tuned in a wide range, i.e., Y_M of 11-615 MPa, E_B of 3-420%, and moisture uptake of 0.5-15.1 wt%. *In vitro* and *in vivo* screening of these WBPUs indicated that higher Y_M (> 150 MPa) is preferred in order to achieve good hold of an

initial style, and that the optimal E_B is 15-300%, outside of which polyurethane materials became either too brittle (E_B < 15%) or too elastic (E_B > 300%); as a result, the hair feels either very stiff or very gummy. The U_S for all WBPUs falls in the range of 3-26 MPa. However U_S does not seem to have a strong correlation with WBPU styling performance. Our initial screening shows that polyurethane films with a moisture uptake of < 10 wt% exhibit superior humidity resistance *in vitro* and *in vivo*. Therefore the optimal WBPU properties for hair styling applications were determined to be: Y_M > 150 MPa, E_B: 15-300%, and moisture uptake < 10%.

To improve the sensory properties of WBPUs for hair applications, emollient additives were encapsulated in WBPU dispersions. To the best of our knowledge, this concept has not been explored, although vegetable oils containing fatty acids are known to have beneficial effects for hair.[17, 18] Fatty acids are the ideal additives for this purpose because they are naturally-occurring, renewable, and versatile in structures—the aliphatic fatty acid chain length can vary between 8 and 24 carbons and include up to 5 double bonds.[18] A preliminary screen of seven saturated fatty acids with varying aliphatic chain lengths from 10 to 22 (C10:0 to C22:0) showed that upon encapsulation at a 2 wt% concentration, most additives had minimal impact on WBPU particle size, morphology, or mechanical properties. However, as expected, a strong correlation was observed between the aliphatic chain length and the moisture uptake of cast polyurethane films.[19] **Figure 2** shows that as the aliphatic chain length increased from 10 to 22 carbons, the moisture uptake gradually decreased from 7.1 wt% to 5.5 wt%, suggesting that fatty acids with longer aliphatic chains should be used in order to obtain hydrophobic WBPUs. One disadvantage of saturated fatty acids is that they are all solids and hence are difficult to incorporate during synthesis. For this reason, unsaturated fatty acids of similar chain lengths in liquid form are studied.

The unsaturated derivatives of stearic acid (C18:0) were also explored—oleic (C18:1), linoleic (C18:2), and linolenic (C18:3) acids. Encapsulation of the fatty acids during the pre-polymer stage of the WBPU synthesis (i.e., prepolymer encapsulation) at 2 wt% concentration had no significant effect on the mechanical properties or moisture uptake of the cast polyurethane films; however, the viscosities of the final WBPU dispersions decreased as the degree of unsaturation increased (**Table 1**). Since these unsaturated fatty acids did not negatively impact the WBPU mechanical properties or moisture uptake, they can each potentially be encapsulated in the WBPU for hair styling applications. It is known, however, that the rate of fatty acid oxidation increases by at least a factor of one with the addition of each degree of unsaturation.[20] Preliminary stability screening showed that although WBPU dispersions containing C18:3, C18:2, or C18:1 were more stable than dispersions containing C18:0, the dispersion containing C18:3 turned yellow at room temperature over time, likely due to slow oxidation. In comparison, WBPUs incorporated with C18:2 were found to be stable for a long period of time (≥ 12 weeks at room temperature) without any sign of oxidation, and were therefore the most preferred.

To study the effect of additive concentration, C18:2 was incorporated into batches of the preferred WBPU at 0.75, 2, and 5 wt%. Interestingly, no measurable differences were observed in moisture uptake, molecular weight, or primary particle size within this concentration range (**Table S3**). XRD analysis also showed similar peak profiles and intensities for WBPUs with and without C18:2 (**Figure 3a**, PU-IPDI vs. PU-LA-2P and PU-LA-5P), suggesting incorporation of the additive up to 5 wt% did not change the polymer crystal structure or crystallinity. Mechanical testing, however, revealed a significant plasticization effect at 5 wt% C18:2 **(Figure 3b**, PU-LA-5P**)**. The optimal additive concentration was thus determined to be 0.75-2 wt%.

Because they exist in liquid form, unsaturated fatty acids can also be incorporated into chain-extended polyurethanes after water addition and particle formation (i.e., dispersion encapsulation). **Table 2** shows that mechanical properties, moisture uptake, molecular weight, and primary particle size were not affected by the timing of additive encapsulation. WBPUs containing C18:2 synthesized using either the pre-polymer or dispersion encapsulation methods contained well-defined 25-30 nm nanoparticles (**Figure S3a-b**). However, TEM images of WBPUs containing C18:1 revealed key differences—the WBPU prepared via pre-polymer encapsulation contains aggregated chain-like structures (**Figure S3c**), while the dispersion obtained via dispersion encapsulation comprises well-dispersed spherical particles (**Figure S3d**). Because it consistently yields no adverse effects to the physicochemical properties of WBPUs, the dispersion encapsulation method is preferred.

The stability of all WBPU dispersions was evaluated under accelerated aging conditions at 40 °C for 12 weeks, conditions which translate to 2-3 years of shelf life at room temperature.[21] Compared to commercially available WBPUs used in personal care applications, the WBPUs discussed herein demonstrated superior long-term stability. **Figure 4** shows that there are no changes in color, opacity, or viscosity for two representative WBPUs, PU-IPDI and PU-LA-2P after the 12-week accelerated aging procedure. By contrast, the two commercial resins investigated, Commercial Resin #1 (CR1, **Table S4**) and Commercial Resin #2 (CR2) gelled after 6 and 8 weeks, respectively. Commercial Resin #2 also contained significant precipitation prior to accelerated aging. The observed stability differences may be correlated to differences in particle size distribution, and degree of aggregation. TEM analysis reveals that the WBPUs synthesized herein remained well dispersed throughout the accelerated aging process with no noticeable change in primary size (39 ± 10 nm) (**Figure 4bi-iv**). By contrast, CR1, although composed of particles with similar initial size as

our WBPUs, became aggregated under accelerated aging conditions, leading to the formation of highly crosslinked structures and ultimately gelation after 6 weeks (**Figure 4bv, vi**). Although CR2 did not show any changes in primary particle sizes, it also gelled up after 8 weeks of aging at 40 °C (**Figure 4bvii, viii**). The poor stability of CR2 likely arose from its inherent heterogeneity and the presence of much larger particles.

Figure 5a shows the mechanical properties of select WBPUs with optimal mechanical properties and moisture uptake (filled markers) as well as suboptimal commercial resins outside of this target property "zone" (open markers). Only the WBPUs with optimal mechanical properties (Y_M and E_B) will provide a curl with durability in the presence of everyday mechanical manipulations such as combing or touching the hair. Furthermore, hair styled using hydrophobic WBPUs (moisture uptake < 10 wt%) is more resistant to changes in ambient humidity, resulting in style longevity. When a WBPU possesses all three of these properties, the performance *in vitro* and *in vivo* is improved. **Figure 5b** shows the *in vitro* curl retention behavior of hair tresses prepared using WBPUs with optimal properties (PU-IPDI-1 and PU-IPDI-2, **Table S1**) as compared to those without optimal properties (CR3 and CR4, **Table S4**). When these curled tresses were exposed to elevated relative humidity (75% RH) for 180 minutes, the ones treated with the WBPUs in the target "zone" maintained their shape better than those treated with WBPUs without the optimal properties. The *in vivo* study shown in **Figure 5c** also illustrates the difference in curl and style retention for WBPUs with and without the optimal mechanical properties and water uptake. The left side of the panelist's head treated with an optimal WBPU shows significantly improved style retention over 3 min exposure to high humidity in comparison to the right side treated with the suboptimal CR3. Due to the synthesis and processing optimization discussed previously, the WBPUs provided superior *in*

vitro and *in vivo* sensory and curl retention performance when applied to the hair. **Figure 5d** shows

that when C18:2 is encapsulated during the synthesis process, the natural-feel sensory benefits in

the final styling products is further improved. Altogether, *in vitro* and *in vivo* testing demonstrated

that WBPUs with optimal properties are promising materials for developing strong, long-lasting

styling products with natural feel.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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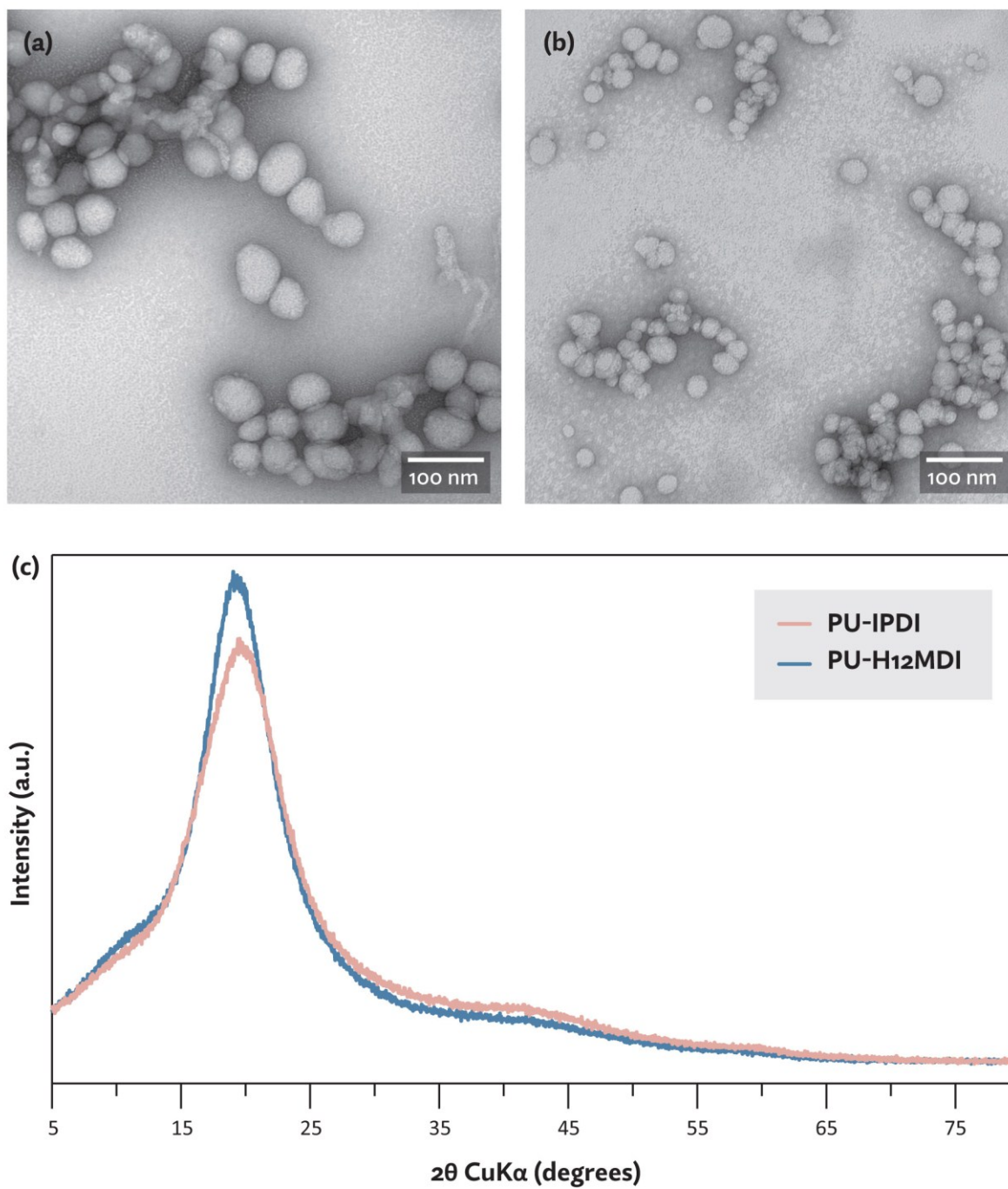
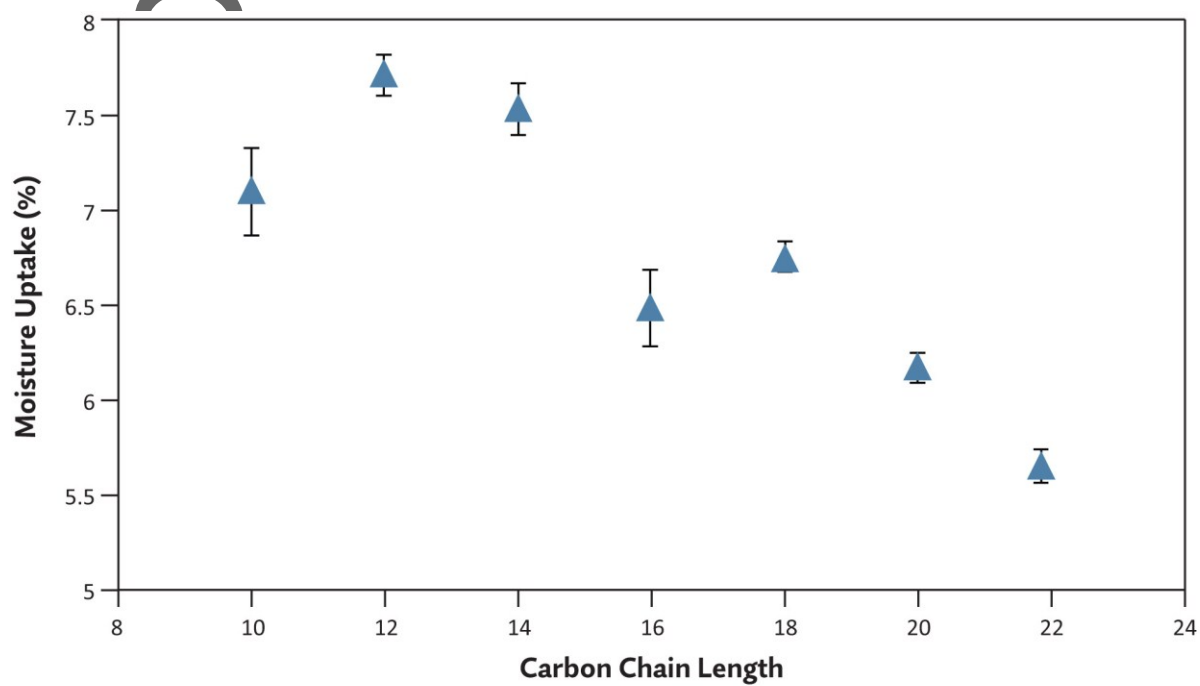**Figure 1:** (a-b) TEM images of WBPUs prepared using (a) H_{12}MDI or (b) IPDI; (c) XRD patterns of WBPUs prepared using both isocyanate groups.

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Figure 2. Moisture uptake of WBPU dispersions incorporated with saturated fatty acids of different carbon chain lengths.
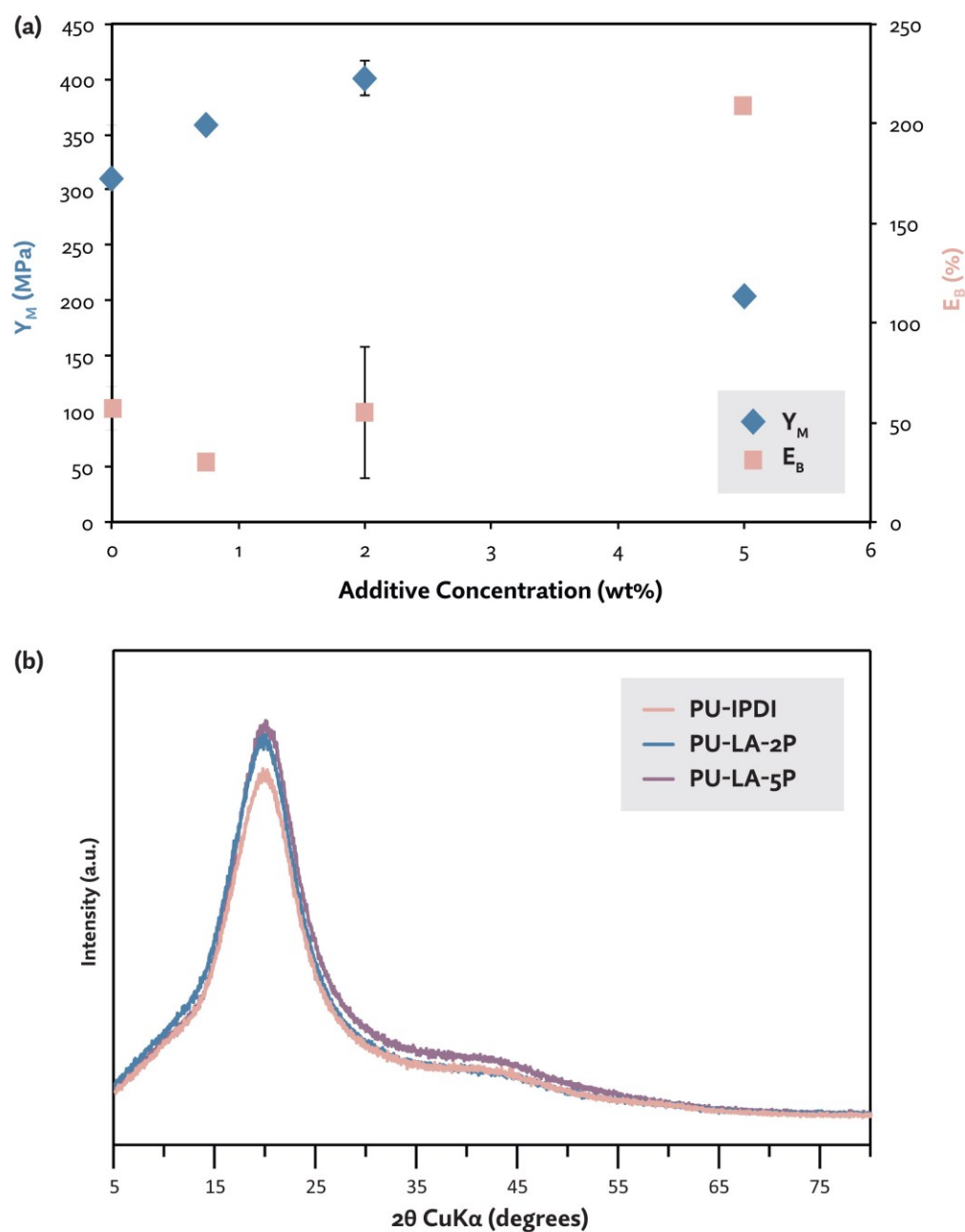
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Figure 3. (a) Mechanical properties (Y_M and E_B) and (b) XRD patterns of WBPU dispersions encapsulated with linoleic acid at different additive concentrations.
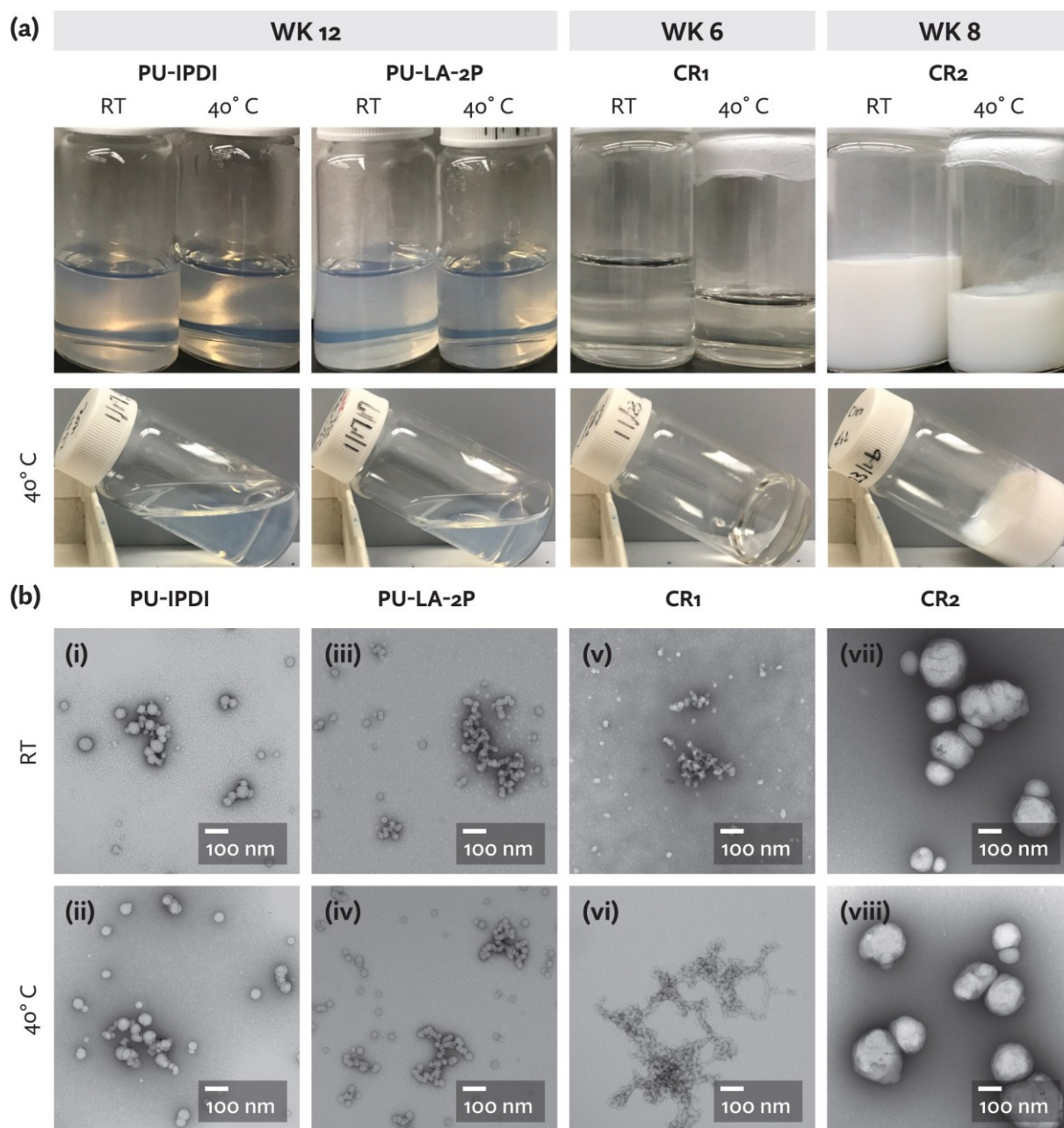
Figure 4. (a) Physical appearance of waterborne polyurethane with and without additive and two commercial resins. (b): TEM images of RT and aged polyurethane samples.
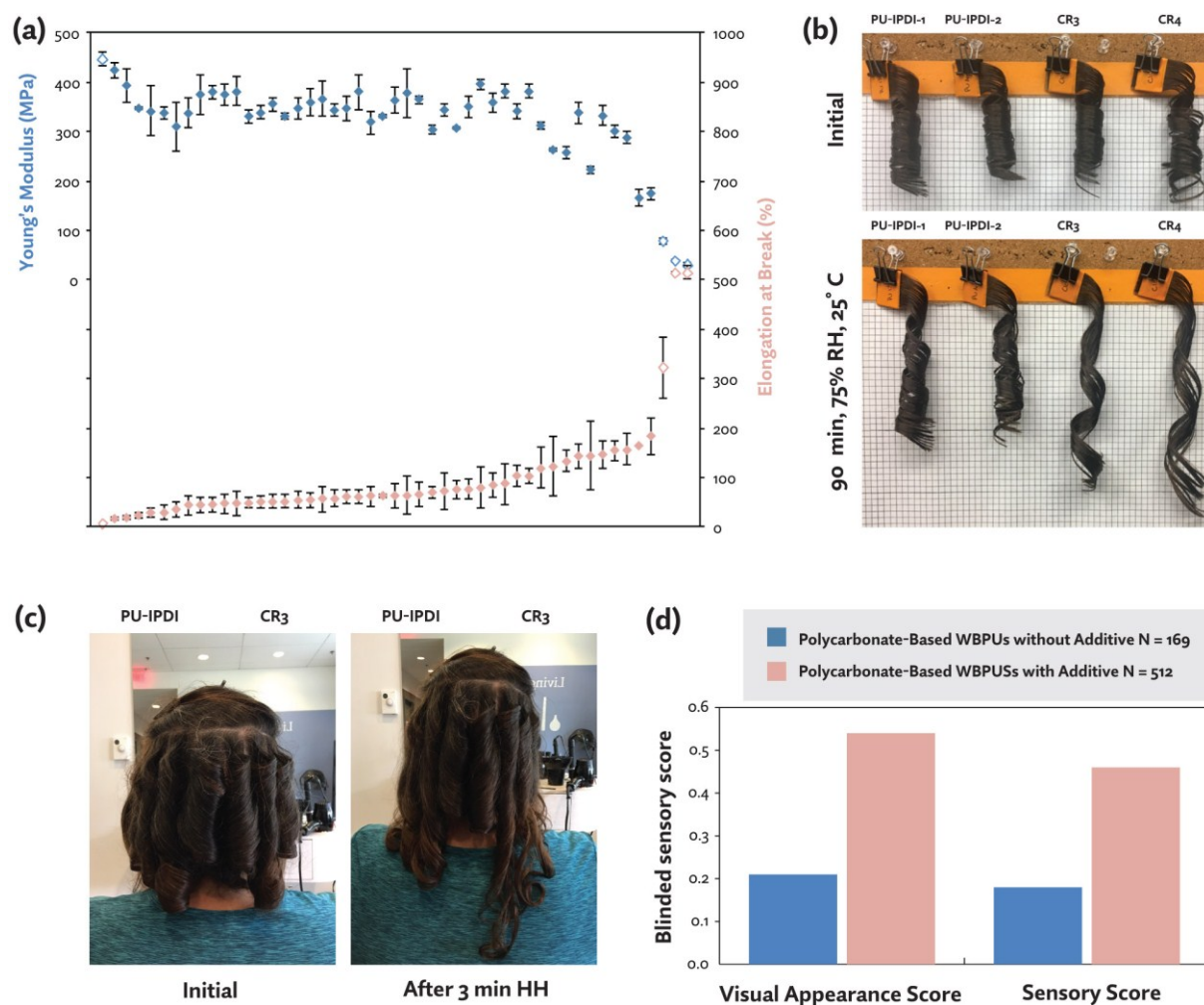
Figure 5. (a) Mechanical properties and *in vitro* and *in vivo* performance of optimal WBPUs (Y_M >150 MPa, E_B: 15-300%, filled markers) and commercial resins (open markers). (b) *In vitro* curl retention of hair tresses treated either with WBPUs having optimal properties (PU-IPDI-1, PU-IPDI-2) or commercial WBPUs (CR3, CR4), and then equilibrated at elevated humidity (75% RH) for 90 minutes. (c) *In vivo* curl retention of hair treated with either a WBPU having optimal properties (PU-IPDI) or a commercial WBPU without the optimal properties (CR3), followed by 3 min exposure to high humidity (d) Blinded sensory scores for tresses treated with polycarbonate-based WBPUs with or without functional additives.

Table 1. Physicochemical properties of WBPU dispersions encapsulated with additives of different degrees of unsaturation.
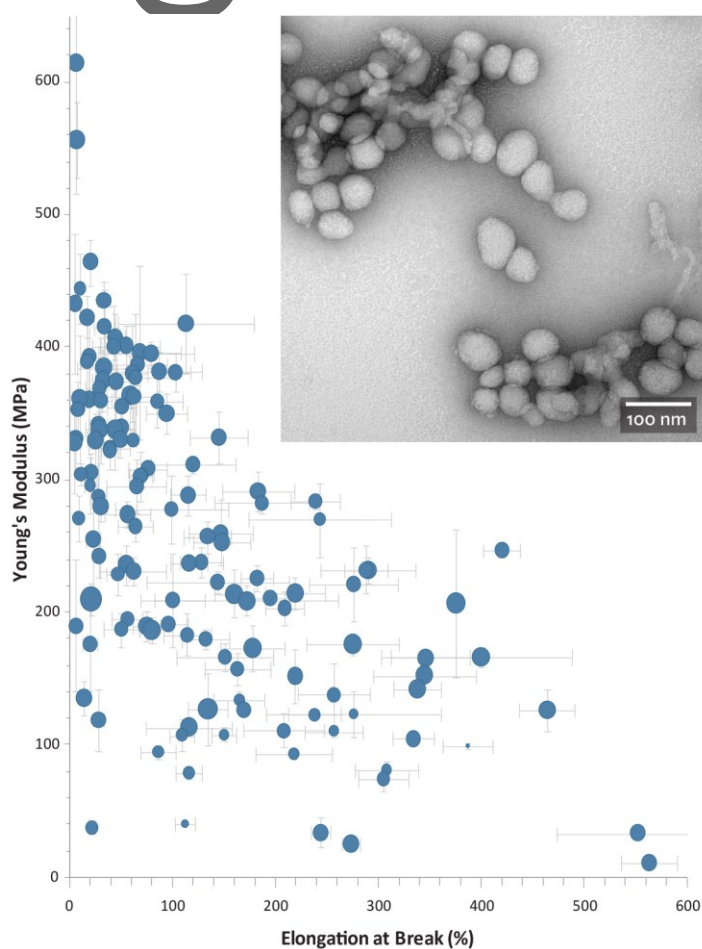
WBPU	Additive	Y_M (MPa)	E_B (%)	Moisture uptake (%)	M_w (Da)	M_n (Da)	Primary Size (nm)	Viscosity (cP)
PU-SA-2P	Steric Acid	176 ± 36	20 ± 7	6.77 ± 0.08	27300	10200	26.9 ± 2	>2 M
PU-OA-2P	Oleic Acid	332 ± 20	145 ± 28	6.74 ± 0.21	29600	10700	30.5 ± 7.4	3515
PU-LA-2P	Linoleic Acid	401 ± 16	55 ± 33	7.12 ± 0.15	26000	9700	25.1 ± 3.8	998
PU-LNA-2P	Linoleic Acid	355 ±14	51 ± 14	6.67 ± 0.06	29300	9900	NA	34
PU-IPDI	N/A	310 ± 41	57 ± 49	6.58 ± 0.59	31400	8900	27 ± 3.6	35

Table 2: Physicochemical properties of WBPU dispersions with encapsulated fatty acids using two different processing routes: prepolymer and dispersion.

WBPU	Additive	Encapsulation Route	Y_M (MPa)	E_B (%)	Moisture uptake (%)	M_w (Da)	M_n (Da)	Primary Size (nm)
PU-OA-2P	Oleic Acid	Prepolymer	332± 20	145 ± 28	6.74 ± 0.21	29600	10700	30.5 ± 7.4
PU-OA-2D	Oleic Acid	Dispersion	308 ± 3	76 ± 19	6.55 ± 0.04	26300	9400	28.1 ± 4.6
PU-LA-2P	Linoleic Acid	Prepolymer	401 ± 16	55 ± 33	7.2 ± 0.15	26000	9700	25.1 ± 3.8
PU-LA-2D	Linoleic Acid	Dispersion	374 ± 41	45 ± 16	7.63 ± 0.14	34900	10400	27.1 ± 2.9
PU-IPDI	N/A	N/A	310 ± 41	57 ± 49	6.58 ± 0.59	31400	8900	27 ± 3.6

Through the synthesis of over 300 waterborne polyurethane (WBPU) materials, we have identified the roles of key components that govern WBPU physicochemical properties. Using hair styling as an example, we demonstrated that only the WBPUs with Young's modulus > 150 MPa, elongation at break of 15-300%, moisture uptake < 10% can achieve strong styling performance.